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Indian Standard

IS 12889 : 2018

तरल व्याप्ति परीक्षण के लिए इस्तेमाल सामग्री का प्रदर्शन मूल्यांकन

(पहला पुनरीक्षण)

Performance Evaluation of Materials Used for Liquid Penetrant Test

(First Revision)

ICS 19.100

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भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुरशाह ज़फर मार्ग, नई दिल्ली–110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002
www.bis.org.in www.standardsbis.in

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FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Non-destructive Testing Sectional Committee had been approved by the Metallurgical Engineering Division Council.

This standard was originally published in 1989 and with the experience gained over these years, the need for alternate testing method for determination of Ionic Chloride contents has arisen as certain dyes do not get decolorized by ISO AmylAlcohol method. In addition the clause pertaining to other test requires modifications which are also incorporated.

For the purpose of deciding whether particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 ‘Rules for rounding off numerical values (*revised*)’. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

PERFORMANCE EVALUATION OF MATERIALS USED FOR LIQUID PENETRANT TEST — SPECIFICATION

(First Revision)

1 SCOPE

This standard covers materials used for the liquid penetrant test of metals, non-porous ceramics and plastics parts (if compatible) to find out the existence of any discontinuity open to the surface. The temperature of the part under examination shall be in between 15°C to 50°C.

2 REFERENCES

The following standards contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
1070 : 1992	Reagent grade water — Specification (*third revision*)
5522 : 2014	Stainless steel sheets and strips for utensils (*third revision*)

3 PENETRANT MATERIALS

The term penetrant materials shall include cleaning agents, penetrants, penetrant removers (solvents), emulsifiers, developers, etc, used in the examination process.

4 CLASSIFICATION

4.1 Penetrants

4.1.1 The penetrant inspection materials shall be of three groups. The group denotes the family of penetrant system. The groups are classified by the visibility of discontinuities when exposed to white light or black light.

a) Group I — Visible
b) Group II — Fluorescent
c) Group III — Visible and fluorescent (dual mode)

4.1.2 The test methods are classified by the removability of the penetrants.

a) Method A — Water washable
b) Method B — Post emulsifiable (lipophilic or hydrophilic)
c) Method C — Solvent removable

4.2 Developers

a) Dry developer;
b) Non-aqueous wet developer; and
c) Aqueous wet developer.

4.3 Solvent Removers

Solvent removers covered by this standard shall be of the following classes:

a) Class I — Halogenated
b) Class II — Non-halogenated

5 PHYSICAL PROPERTIES OF PENETRANT MATERIALS

5.1 Toxicity

All penetrant materials shall have no adverse effect on the health of personnel when used for its intended purpose. However, use of proper personal protective devices and conducting the test in well-ventilated area is recommended.

5.2 Corrosive Properties

All items included in each group of materials shall be non-corrosive and non-tarnishing. Metal strips of aluminium, copper, yellow brass, mild steel and stainless steel of approximate dimension 100mm × 25 mm shall be kept immersed in various products for a minimum period of 48 h. The test shall be carried out at the ambient temperature between 15°C and 45°C. The metal strips shall show no evidence of pitting, etching, cracking or tarnishing when examined using 10× magnification. Corrosion test may be carried out on any other material, if required by the user.

5.3 Flash Point

For all penetrants and lipophilic emulsifiers, intended for use in open tanks or open containers, the minimum flash point shall be 50°C. The flash point shall be measured by Abels Closed Cup or Pensky Martin Closed Cup Method as applicable.

In case of penetrant materials packaged in aerosol cans, since the containers may contain flammable hydrocarbon gases or gases with low flash points, the containers shall be labeled suitable by including such warnings as necessary either in writing or by suitable logos. The flash point measurement is not applicable to the penetrant materials supplied in aerosol cans.

5.4 Fluorescent Brightness

Fluorescent brightness shall be adequate for use.

5.5 Storage Stability

The storage stability shall be certified by the manufacturer as per the following procedure. A filled and closed container of each item of a family shall be stored for one year at the temperature range of 15°C to 50°C without exposure to direct sunlight. At the end of the storage period, the material shall be subjected to the quality conformance tests as applicable to the item given in Table 1.

Table 1 Quality Conformance Test
(*Clause* 5.5)

Test	Reference
Flash point	5.3
Developer fluorescence	9.0
Temperature stability	7.0
Water tolerance	8.0
Reentrant removability	Annex A
Developer removability	Annex B
Net content of aerosol containers	Annex C

Visual examination of the container shall also be done to see if the penetrants or the products stored have had any deleterious effects (corrosion) on the container.

5.6 Penetrant Removability

Removability test of penetrant is performed as per Annex A. The penetrant shall leave substantially no more residual penetrant than left by reference sample.

6 CONTROL OF CONTAMINANTS

6.1 All the penetrant materials used on nickel based alloys and austenitic stainless steel shall be analyzed for sulphur content as per Annex E as they have been found to be subject to corrosion and embrittlement by contact with sulphur in the form of sulphate ions at elevated temperature.

6.2 All penetrant materials used on austenitic stainless steel and titanium based alloys shall be analysed for ionic halide content for the same reason stated in **6.1.**

6.3 For general applications, the values for total sulphur and halide content shall not exceed 1.0 percent each by weight for special applications, such as, in nuclear, space, etc, the values for total sulphur and ionic halide content shall not exceed 500 ppm and 25 ppm respectively.

7 TEMPERATURE STABILITY

The temperature stability of the penetrant shall be tested by subjecting 50 ml of the penetrant in a closed glass tube to two complete cycles of the temperature ranging from 10°C to 55°C. Each cycle shall extend over a minimum time period of 8 h. After the temperature cycling has been completed, the material shall be allowed to return to room temperature. The samples shall be visually examined at room temperature for any precipitation and separation of constituents. In case, sample is tested at different temperature range, the manufacturers shall state the range in which the penetrant materials have been tested and found acceptable.

8 WATER TOLERANCE

This process is applicable for water washable penetrant and lipophilic emulsifier materials used in tank type system. 50 ml of material under test shall be taken in a 100 ml glass beaker and 0.5 ml of water is added at a time, using a burette and after each addition the solution is shaken well. This process is repeated till the endpoint is reached when the test material turns cloudy or thickens or coagulates. The amount of water added in percentage of test material gives the water tolerance for test material. The water tolerance can be calculated by the formula.

$$\text{Water Tolerance} = \frac{B}{50+B}\times 100$$

where

B = burette reading in millimetre.

The manufacturers shall specify the water tolerance of their products.

9 DEVELOPERS

All developers, dry or wet, shall provided a good contrasting white background to the penetrant for which it is intended. Developers shall not exhibit fluorescence when exposed to black light of 365 nanometer wave length. All developers shall be easily and completely removed from the test surface according to the procedures given in Annex B.

9.1 Dry Developers

9.1.1 Dry developers shall be light, fluffy and free from moisture and lumping.

9.1.2 The bulk density of the developer powder shall be less than 0.2 g/cc. To measure the density of dry developers, one litre beaker shall be accurately weighed and the weight recorded. The beaker shall then be filled with the dry developer, which has been heated to 105°C for 1 h. The beaker is tapped lightly on the side, to cause settling of the developer. The edge of a 'spatula' or other suitable instrument shall be scrapped across the top of the beaker in such a manner that the surface of the developer is in level with the top of the beaker. The filled beaker shall then be accurately weighed. The weight of the empty beaker shall be subtracted from the total weight of the developer obtained shall not be more than 200 g.

9.2 Non-Aqueous Wet Developers

9.2.1 Non-aqueous wet developers shall be solids suspended in non-aqueous liquid. They shall be ready-mixed in pressurized or non-pressurized containers. Each container shall be provided with a pallet to aid in agitation of the material and to indicate proper mixing.

9.2.2 To check the precipitation rate, the settling rate test may be performed as given below:

> Shake the non-aqueous wet developer well. A 50 ml of material shall then be poured into a 50 ml stopper-graduated cylinder. Shake the material well and keep the cylinder in a rest position. Developer powder will start settling. Start the stopwatch as soon as level of developer powder crosses the 50 ml mark of the cylinder. Measure the settling time for every 5 ml volume of settled developer powder up to total 25 ml of settled developer powder. The value of settling period should be near to the value declared by the manufacturer in their specification.

9.3 Aqueous Wet Developers

9.3.1 The aqueous wet developers shall be supplied in wet or dry condition. Instructions for mixing shall be provided by the manufacturer.

9.3.2 The water soluble developer shall be mixed in accordance with the manufacturer's instructions. A 25 ml of solution shall then be poured into a graduated measure and allowed to stand for 4 h. After this, when visually examined, no precipitation shall be observed.

10 SOLVENT REMOVERS

Solvent removers may be suitable commercial formulations or proprietary formulations prepared from suitable solvents and shall be identified by the manufacture as to which class they belong to. Solvent removers shall not leave any residual penetrant on the test surface. In addition, they shall also not leave any oily residue.

11 BLACK LIGHT

Black light used for fluorescent penetrant inspection shall emit ultra-violet radiation having wavelength in the range of 330 nm-380 nm. The intensity of black light on the test surface shall be a minimum of 800 microwatts/cm^2 in a circle of diameter 75 mm when held at a distance of 30 cm. the intensity of black light shall be measured by a calibrated ultra-violet meter.

12 SYSTEM SENSITIVITY PERFORMANCE

12.1 Nickel-chromium (Ni-Cr) test panels manufactured by reputed manufacturers and provided with the calibration test certificates, indicating the size of the defects with appropriate photographs shall be used for sensitivity evaluation. Based on the visibility of the cracks and the type of panels, sensitivity of the penetrant system can be classified as follow:

System Sensitivity	*Type of Test Panels*	*Crack Depth × Width*
Low	Coarse Grade	50.0 × 2.0 µm (approx)
Low Medium	Medium Grade 1	30.0 × 1.0 µm (approx)
High Medium	Medium Grade 2	20.0 × 1.0 µm (approx)
Ultra High	Fine Grade	10.0 × 1.0 µm (approx)

The supplier shall specify sensitivity level of the penetrant system. However, if not specified, visible penetrant system shall be tested using coarse grade panel (50.0 × 2.0 µm) whereas, fluorescent penetrant system shall be tested using medium grade '2' panel (20.0 × 1.0 µm).

12.2 Use of Test Panels for Comparison

Nickel-chromium (Ni-Cr) test panels can also be used for comparing the two penetrants in the following way. Each penetrant is placed on the separate section of the nickel-chrome panels. If both the sections are on the same piece of the test panels, care should be taken to avoid any mixing of the two penetrants. This can be simply achieved by covering the unused section by a piece of paper while penetrant or developer is being applied over the other section. Based on the established procedures, the sequence of application and general processing shall be identical, such as, penetrant dwell, removal and developing. The two sections shall be compared for:

a) Completeness of crack patterns;
b) Sharpness of crack delineation, that is, definition;

c) Brilliance; and
d) Contrast.

12.3 Re-use of Test Panels

12.3.1 Visible and fluorescent dye penetrants shall be tested on separate test panels. In case, the same panels are to be used for both the penetrants, the panels shall be thoroughly cleaned before reuse.

12.3.2 Since contaminating effect is likely to occur whenever tests are made, panel shall never be reused without post cleaning after each test by soaking the panel in acetone for 15 to 30 min followed by drying in oven at 80°C maximum or natural drying.

12.4 Test for Penetrants only

12.4.1 *Meniscus Spot Test for Sensitivity*

The method employs a plano-convex lens of 1.06 m radius, placed upon an optically flat glass plate or a white tile. A few drops of penetrant are put on the plate or tile and lens is kept on it so that the penetrant fills the space for some distance out from the point of contact. At the point of contact, the thickness of penetrant films approaches zero and due to this, a colourless spot appears around this point. Spot diameter, when measured by scale having graduation of 0.5 mm, shall not exceed 4.0 mm and 2.5 mm for colour contrast penetrants and fluorescent penetrants respectively. The black light intensity for viewing fluorescent penetrants shall not be less than 800 µW/cm^2 and it should be kept constant during the measurement as the spot diameter varies with the incident light intensity.

12.4.2 *Colour Stability Test*

The fluorescent dyes have tendency to lose their ability to fluorescence after exposure to ultraviolet or black light. In addition to the sensitivity test, the same set up can also be used for testing the colour stability of fluorescent penetrants. The spot diameter shall not increase when the fluorescent penetrant under the lens is exposed to black light of constant intensity 3 000 µW/cm^2 for 1 h.

13 PACKING AND LABELLING

13.1 Net Material Content of Aerosol Container

Net material content of aerosol container shall be measured as per Annex C.

13.2 The label on containers of penetrant material shall bear:

a) Net content in grams,
b) Classification of penetrant material,
c) Manufacturer's instructions for use,
d) Batch or lot number,
e) Month and year of manufacture and expiry,
f) Storage instructions,
g) Statutory warning, if applicable,

ANNEX A

(*Cluase* 5.6)

REMOVABILITY/WASHABILITY TEST FOR PENETRANTS (BY METHOD A AND METHOD C)

A-1 REMOVABILITY TEST FOR SOLVENT REMOAVLE PENETRANTS

A-1.1 Penetrant of these groups shall be removable by wiping with a cloth dampened with penetrant remover.

A-1.2 The penetrant removability shall be tested on a fairly rough surface, such as austenitic stainless steel panels (*see* IS 5522) of 100 mm × 50 mm × 1.6 mm in size and shot-blasted with 150 micrometer average size grit, using 2.5 kg/cm^2 of air pressure with a gun held at approximately 500 mm from the panels for about 10 min. Prior to use, the panels shall be vapour degreased, heated to 100°C and cooled to room temperature in a desiccator. Alternatively the TAM Panel may be used.

A-1.3 The removability of penetrants of these groups shall be tested by pouring approximately 5 ml of the sample on centered spot 40 mm from the top of the panel. The panel shall be kept inclined at 45° and allowed to drain for 15 min. At the end of the drain period, the panel shall be wiped with a dry cloth to remove the surplus penetrant, after which it shall be wiped with a cloth dampened with penetrant remover and dried. The developer from the manufacturer shall be applied and the panel examined under white or black light as appropriate. The penetrants shall not leave any background, which may interfere with the interpretation of indication.

A-2 REMOVABILITY TEST FOR POST EMULSIFIABLE PENETRANTS

A-2.1 The penetrants shall be tested as specified in **A-1.3** except after the penetrant drain period, the panel shall be dipped in the applicable emulsifier until the penetrant is covered.

A-2.2 The emulsifier shall have an appropriate dwell time as specified by the manufacturer or as determined by the experience and the panels shall be washed using a special washing fixture, in accordance with the standard washing procedure as per Annex D. The panels are dried, coated with applicable developer and examined under white or black light as appropriate. The penetrants shall not leave any background, which may interfere with the interpretation of indication.

ANNEX B

(*Clause* 9 and *Table* 1)

REMOVABILITY TEST FOR DEVELOPER

B-1 TEST PANELS

Test panels for this test shall be prepared in accordance with **A-1.2**.

B-2 DRY DEVELOPERS

Coat the panel with the developer by dusting and allow to stand for 5 min. Place the panel in the wash fixture and wash for 1 min in a cold tap water spray at the pressure of 30 pounds per square inch gauge (1 pisg = 6 894.7 pa). Panel shall be air-dried and examined under oblique illumination and shall show no trace of developer.

B-3 AQUEOUS AND NON-AQUEOUS DEVELOPERS

The suspensions or solutions, as appropriate, mixed in accordance with the manufacturer's instructions, shall be applied to completely cover the test panel. The panel shall be dried suitably. After drying, the panel shall be placed in the wash fixture and washed for 1 min with a cold water spray at 30 psig. The panel shall be air-dried and examined under oblique illumination and shall show no trace of developer.

ANNEX C

(*Clause* 13.1 and *Table* 1)

DETERMINATION OF NET CONTENT OF AEROSOL CONTAINERS

C-1 Remove valve protective caps and check the gross weight to the nearest 2.0 g of each of the 10 containers selected at random from each product in the family to determine the lightest and heaviest package in the sample lot. Record the gross weight of the lightest and heaviest container.

C-2 Choose the lightest container and shake well.

C-3 Empty the lightest container by pressing the valve actuator until no additional product or gas is expelled. If any product remains, it should be expelled as completely as possible. Adequate safety precautions for fire hazard shall be used during expulsion of the propellant gas.

C-4 Weigh the empty container to determine the wet tare weight (weight of the container plus any product not expelled).

C-5 The net content of Aerosol container is determined by difference in weight of filled and empty container.

NOTE — To be carried out by the manufacturer.

ANNEX D

(*Clause* A-2.2)

STANDARD WASHING PROCEDURE AND ITS EQUIPMENT

D-1 Panels used for various washability tests shall be washed as per the following standard washing procedure.

During washing, panel shall be kept at 45° on a stand. An even curtain of water shall be allowed to flow over the surface from the top of the panel for a definite length of time at a controlled low pressure (approximately 30 psig).

D-2 A special fixture may be devised for standard washing procedure. One such washing fixture is described here. It contains one rectangular tank mounted at the top of the fixture. Tank is hinged at the bottom so that it can be tilted for drainage. Number of valves is fixed to the tank at its bottom that allows uniform flow of water over entire width of the panel. Below the valves, panel can be kept at 45° on a stand, for draining as well as washing.

ANNEX E

(*Clause* 6.1)

PROCEDURE FOR DETERMINATION OF CHLORIDE AND SULPHUR CONTENT

E-1 DETERMINATION OF LEACHABLE CHLORIDE

E-1.1 Principle

This method is applicable for the determination of leachable chloride. Sample is a treated with isoamyl alcohol, leachable chloride is extracted with water and estimated by spectrophotometer.

NOTE — Follow manufacturer's instruction for operation of the spectrophotometer.

E-1.2 Stock Solution

a) Deionized water,

b) Isoamyl alcohol,

c) 10 percent silver nitrate (Dissolve 10 g of silver nitrate in 100 ml of deionized water. Store in amber coloured bottle),

d) Conc. Nitric acid.

e) 1:1 Nitric acid (Dilute 50 ml of AR grade concentrated Nitric acid to 100 ml with deionized water),

f) Chloride Standard of 10 µg/ml (use sodium chloride) prepared as below:

Take 2.648 g of sodium chloride and make up to 1 000 ml with deionized water; it gives 1 000 µg/ml stock solution (Solution A). Dilute 10 ml of this solution (Solution A) to 1 000 ml with deionized water to give working standard solution of 10 µg/ml (Solution B).

E-1.3 Procedure

a) In a weighing bottle take nearly one-third or approximately 10 ml of isoamyl alcohol. Weigh the bottle (W_1).

b) To this add 2.0 to 2.5 ml sample, note the weight of the sample, mix well and transfer into 120 ml separating funnel. The weight of the sample is given by W_2–W_1. In which W_2 represents the weight of the bottle with isoamyl alcohol and sample.

c) Rinse sample bottle with about 10 ml isoamyl alcohol and transfer into separating funnel.

d) Add 20 ml of deionozed water and extract for 5 min.

e) Add drop by drop 1:1 nitric acid, if separation of layer does not take place properly.

f) Collect bottom aqueous layer in a volumetric flask of 50 or 100 ml capacity.

g) To separating funnel again add 20 ml of deionized water and extract for 5 min.

h) Collect bottom aqueous layer. Make up solution in volumetric flask of 50 ml capacity if the solution is clear. If the aqueous phase solution is coloured, extract the aqueous phase with 10 ml of isoamyl alcohol. Repeat this step if the colour persists. If the aqueous solution is turbid as in the case of developer solution filter the solution till the filtrate is clear and free from turbidity. Make up the solution to 50 ml, take a suitable aliquot and add to that 2 ml nitric acid and 2 ml silver nitrate (silver nitrate is added just before taking readings). Make up the solution to 25 ml.

j) Sample readings are compared with standard values by taking absorbance using a spectrophotometer. Follow manufacturer's instructions for the use.

k) Carry out an experiment using all the solutions as in the case of sample but omitting the sample. Determine the process blank and subtract it from the sample reading.

m) Calculation:

$$\text{Chloride, ppm} = \frac{(A_2 - A_1)\times V_1}{V_2 \times M}$$

where

A_1 = µg total of chloride in the process blank solution,

A_2 = µg total of chloride in the sample solution used for measurement,

V_1 = volume of the solution,

V_2 = volume of the sample aliquot used for the measurement, and

M = mass of sample, in g.

NOTE — Construct a calibration graph of absorbance *versus* total chloride in 25 ml of the solution used for absorbances versus measurement. Use this graph to calculate the total amount of chloride in µg of sample used for analysis (A_2). Calculate similarly the total amount in µg of the process blank (A_1).

E-2 DETERMINATION OF TOTAL SULPHUR

E-2.1 Principle

This method is applicable for the determination of total sulphur. Sulphur in the sample is converted to oxides of sulphur by burning the sample in an oxygen atmosphere. The resulting oxides are converted to sulphate in presence of sodium carbonate containing Hydrogen peroxide. The sulphate is measured by a spectrophotometric method using Barium chloride.

E-2.2 Stock Solution

a) Conditioning Reagent = 10 ml barium chloride + 80 ml water (distilled)+ 10 ml conc. hydrochloric acid + 10 ml glycerol,

b) Sodium carbonate 5 percent (dissolve 5 g of sodium carbonate in 100 ml of distilled water),

c) 1:1 Hydrochloric acid (dilute 50 ml of AR grade concentrated hydrochloric acid to 100 ml with distilled water),

d) Hydrogen peroxide 30 percent AR grade ,

e) Sulphur 20 µg/ml

Take 4.428 5 g of sodium sulphate and make up to 1 000 ml. It gives 1 000 µg/ml stock solution (Solution A). Dilute 10 ml of this solution (Solution A) to 500 ml with deionized water to get solution of 20 µg/ml (Solution B).

E-2.3 Procedure

a) Take a clean bomb calorimeter and to that add 5 ml of 5 percent sodium carbonate and 5 drops of H_2O_2 and mix thoroughly.

b) Tie wire to arms of calorimeter, so as to pass the current.

c) Tie with cotton thread, a filter paper strip that will dip in the crucible where the sample is taken.

d) In a clean silica glass crucible insert the strip of cut filter paper (similar to Whatman Filter paper (No. 40) and to that add 1.0 g of sample and immediately transfer into bomb calorimeter.

e) Fix the cover of the bomb and pressurize it with oxygen gas (25 psi).

f) Pass current so as to ignite the sample and allow the sample to burn.

g) When sample has completely burnt, switch off the current and keep the bomb in a water bath for about half an hour.

h) After half an hour, remove bomb and release the gas pressure.

j) Open the bomb and transfer the liquid inside the vessel into beaker.

k) Wash the crucible lid, side and bottom of the bomb and collect the washing in the same beaker.

l) Sulphur in sample gets oxidized to oxides of sulphur, which then dissolves in sodium carbonate to form sulphate in presence of hydrogen peroxide.

m) Make the solution acidic with 1:1 hydrochloric acid and make up to 50 ml after filtration.

n) Take 25 ml aliquot and add 10 ml conditioning reagent containing $BaCl_2$. Digest on water bath and after cooling make up to 50 ml. Measure the absorbance at 500 nm using distilled water as reference.

p) Take 0.5, 1.0 and 2.0 ml standard sulphate solution (of 20 µg/ml) in 100 ml beaker. Add 10 ml of conditioning reagent containing $BaCl_2$ and digest in a similar manner and after cooling make up to 50 ml. Measure the absorbance at 500 nm using distilled water as reference.

q) Prepare a sample blank using 5 ml sodium carbonate. In all the cases, process the solution as in the case of sample and make up the solution to 50 ml after the addition of 10 ml of Conditioning Reagent containing barium chloride.

r) Calculate the sulphur content in ppm as follows:

$$\text{Sulphur (in ppm)} = \frac{(A_2 - A_1) \times V_1}{V_2 \times M}$$

where

A_1 = µg total of sulphur in the sample process blank solution used for measurement.

A_2 = µg total of sulphur in the sample solution used for measurement,

V_1 = volume of the solution,

V_2 = volume of the sample aliquot used for measurement, and

M = mass of sample, in g.

NOTE — Construct a calibration graph of absorbance *versus* total sulphur in 50 ml of solution used for absorbance *versus* measurement. Use this graph to calculate the total amount of sulphur in µg of sample used for analysis (A_2). Calculate similarly the total amount in µg of the process blank (A_1).

E-3 METHODS FOR MEASURING TOTAL CHLORINE CONTENT IN COMBUSTIBLE LIQUID PENETRANT MATERIALS (ALTERNATE METHOD)

E-3.1 Scope and Application

E-3.1.1 These methods cover the determination of chlorine in combustible liquid penetrant materials, liquid or solid. Its range of applicability is 0.001 to 5 percent using either of the alternative titrimetric procedures. These procedures assume that bromine or iodine will not be present. If these elements are present, they will be detected and reported as chlorine. The full amount of these elements will not be reported. Chromate interferes with procedures, causing low or non-existent end points. The method is applicable only to materials that are totally combustible.

E-3.2 Summary of Methods

E-3.2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The chlorine compounds thus liberated are absorbed in a sodium carbonate solution and the amount of chloride present is determined titrimetrically either against silver nitrate with the end point detected potentiometrically (Method A) or coulorometrically with the end point detected by current flow increase (Method B).

CAUTION — Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blow-out, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 12.7 mm thick or equivalent protection be provided against unforeseeable contingencies.

E-3.3 Apparatus

E-3.3.1 Bomb having a capacity of not less than 300 ml so constructed that it will not leak during the test and the quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly such as the head gasket and lead wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the chlorine content of the liquid in the bomb.

E-3.3.2 *Sample Cup* — Platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside and weighing 10 to 11 g, opaque fused silica, wide-form with and outside diameter of 29 mm at the top, a height of 19 mm, and a 5 ml capacity, or nickel (Kawin capsule form), top diameter of 28 mm, 15 mm in height, as 5 ml capacity.

NOTE — Fused silica crucibles are much more economical and longer-lasting than platinum. After each use, they should be scrubbed out with fine, wet emery cloth, heated to dull red heat over a burner, soaked in hot water for 1 h, then dried and stored in a desiccators before reuse.

E-3.3.3 *Firing Wire* — Platinum, approximately No. 26 B and S gauge.

E-3.3.4 *Ignition Circuit* — It shall be capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

CAUTION — The switch in the ignition circuit shall be of a type that remains open, except when held in closed position by the operator.

E-3.3.5 *Nylon Sewing Thread, or Cotton Wicking,* White

E-3.4 Purity of Reagents

E-3.4.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on analytical reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without reducing the accuracy of the determination.

E-3.4.2 Unless otherwise indicated, references to water shall be understood to mean

referee grade reagent water conforming to IS 1070.

E-3.5 Decomposition

E-3.5.1 *Reagents and Materials*

E-3.5.1.1 Oxygen

It shall be free of combustible material and halogen compounds, available at a pressure of 40 atm (4.05 MPa).

E-3.5.1.2 *Sodium Carbonate Solution* (50 g sodium carbonate per liter) – Dissolve 50 g of anhydrous Na_2CO_3 or 58.5 g of $Na_2CO_3.H_2O$) or 135 g of $Na_2CO_3.10H_2O$ in water and dilute to one litre.

E-3.5.1.3 *White Oil – refined*

E-3.5.2 *Procedure*

E-3.5.2.1 *Preparation of Bomb and Sample* — Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Place 5 ml of sodium carbonate solution in the bomb, place the cover on the bomb and vigorously shake for 15 s to distribute the solution over the inside of the bomb. Open the bomb, place the sample-filled sample cup in the terminal holder, and insert a short length of thread between the firing wire and sample. Use of a sample weight containing over 20 mg of chlorine may cause corrosion of the bomb. The sample weight should not exceed 0.4 g if the expected chlorine content is 2.5 percent or above. If the sample is solid, not more than 0.2 g should be used. Use 0.8 g of white oil with solid samples. If white oil will be used, add it to sample cup by means of a dropper at this time (*see* Notes and caution under **E-3.5.2.2**).

NOTES

1 After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this, is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper coated with a light machine oil to prevent cutting and then with a paste of grit-free chromic oxide and water. This procedure will remove all, but very deep pits and puts a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left out from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from one sample to the other. Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material.

2 If the sample is not readily miscible with white oil, some other non-volatile, chlorine-free combustible diluents may be employed in place of white oil. However, the combined weight of sample and nonvolatile diluents shall not exceed 1 g, some solid additives are relatively insoluble, but may be satisfactorily burned when covered with a layer of white oil.

3 The practice of running alternately samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

E-3.5.2.2 *Addition of oxygen* — Place the sample cup in position and arrange the nylon thread, or wisp of cotton so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the sample from the cup) until a pressure is reached as indicated in Table 2.

CAUTION — Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted.

Table 2 Gauge Pressures

(*Clause* E-3.5.2.2)

Capacity of Bomb, ml	Gauge Pressure, atm (M Pa)	
300 to 350	38 (3.85)	40 (4.05)
350 to 400	35 (3.55)	37 (3.37)
400 to 450	30 (3.04)	32 (3.24)
450 to 500	27 (2.74)	29 (2.94)

NOTE — The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures present a safety requirement.

E-3.5.2.3 *Combustion* — Immerse the bomb in a cold-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least ten minutes. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before again putting it in use (*see* Note 1 under **E-3.5.2.1**).

E-3.6 Analysis, Method A, Potentiometric Titration Procedure

E-3.6.1 *Apparatus*

E-3.6.1.1 *Silver billet electrode*

E-3.6.1.2 *Glass Electrode*, *p*H measurement type.

E-3.6.1.3 *Burette*, 25-ml capacity, 0.05-ml graduations.

E-3.6.1.4 *Millivolt Meter*, or expanded scale pH meter capable of measuring 0 to 220 mV.

NOTE — An automatic titrator is highly recommended in place of items **E-3.6.1.3** through **E-3.6.1.4**. Repeatability and sensitivity of the method are much enhanced by the automatic equipment while much tedious effort is avoided.

E-3.6.2 *Reagents and Materials*

E-3.6.2.1 *Acetone, chlorine-free*

E-3.6.2.2 *Methanol, chlorine-free*

E-3.6.2.3 *Silver nitrate solution (0.0282 N)* – Dissolve 4.791 0 ± 0.000 5 g of silver nitrate ($AgNO_3$) in water and dilute to one litre.

E-3.6.2.4 *Sodium chloride sodium (0.0282 N)* – Dry a few grams of sodium chloride (NaCl) for 2 h at 130 to 150°C, weigh out 1.648 0 ± 0.000 5 g of the dried NaCl, dissolve in water, and dilute to one litre.

E-3.6.2.5 *Sulphuric acid* (1+2) – Mix 1 volume of concentrated sulphuric acid (H_2SO_4, sp. gr 1.84) with 2 volume of water.

E-3.6.3 *Collection of Chlorine Solution*

Remove the sample cup with clean forceps and place in a 400-ml beaker. Wash down the walls of the bomb shell with a fine stream of methanol from a wash bottle, and pour the washings into the beaker. Rinse any residue into the beaker. Next, rinse the bomb cover and terminals into the beaker. Finally, rinse both inside and outside of the sample crucible into the beaker. Washings should we equal but not to exceed 100 ml. Add methanol to make 100 ml.

E-3.6.4 *Determination of Chlorine*

Add 5 ml of sulphuric acid (1:2) to acidify the solution (solution should be acid to litmus and clear of white sodium carbonate precipitate). Add 100 ml of acetone. Place the electrodes in the solution, start the stirrer (if mechanical stirrer is to be used), and begin titration. If titration is manual, set the *p*H meter on the expanded milivolt scale and note the reading. Add exactly 0.1 ml of silver nitrate solution from the burette. Allow a few seconds stirring; then record the new milivolt reading. Subtract the second reading from the first. Continue the titration, noting each amount of silver nitrate solution and the amount of difference between the present reading and last reading. Continue adding 0.1-ml increments, making readings and determining differences between readings until a maximum difference between readings is obtained. The total amount of silver nitrate solution required to produce this maximum differential is the end point. Automatic titrators continuously stir the sample, add titrant, measure the potential difference, calculate the differential, and plot the differential on a chart. The maximum differential is taken at the end point.

NOTE — For maximum sensitivity, 0.002 82 N silver nitrate solution may be used with the automatic titrator. This dilute reagent should not be used with large samples or where chlorine content may be over 0.1 percent since these tests will cause end points of 10 ml or higher. The large amount of water used in such titrations reduces the differential between readings, making the end point very difficult to detect. For chlorine contents over 1 percent in samples of 0.8 g or larger, 0.282N silver nitrate solution will be required to avoid exceeding the 10 ml water dilution limit.

E-3.6.5 *Blank*

Make blank determinations with the amount of white oil used but omitting the sample. (Liquid samples normally require only 0.15 to 0.25 g of white oil while solids require 0.7 to 0.8 g.) Follow normal procedure, making two or three test runs to be sure the results are within the limits of repeatability for the test. Repeat this blank procedure whenever new batches of reagents or white oil are used. The purpose of the blank run is to measure the chlorine in the white oil, the reagents, and that introduced by contamination.

E-3.6.6 *Standardization*

Silver nitrate solutions are not permanently stable, so the true activity should be checked when the solution is first made up and then periodically during the life of the solution. This is done by titration of a known sodium chloride solution as follows: Prepare a mixture of the amounts of the chemicals (sodium carbonate solution, sulphuric acid solution, acetone, and methanol) specified for the test. Pipet in 5.0 ml of 0.028 2 N sodium chloride solution and titrate to the end point. Prepare and titrate a similar mixture of all the chemicals except the sodium chloride solution, thus obtaining a reagent blank reading. Calculate the normality of the $AgNO_3$ solution as follows :

$$AgNO_3(1\ N) = \frac{5.0 \times NaCI\ (1\ N)}{V_A - A_B}$$

where

$AgNO_3(1\ N)$ = normality of the silver nitrate solution,

NaCl(1 N) = normality of the sodium chloride solution,

V_A = millilitres of silver nitrate solution used for the titration including the sodium chloride solution, and

V_B = millilitres of silver nitrate solution used for the titration of the reagents only.

E-3.6.7 *Calculation*

Calculation the chlorine content of the sample as follows:

$$\text{Chlorine (weight percent)} = \frac{(V_S - V_B) \times N \times 3.545}{W}$$

where

V_s = millilitres of silver nitrate solution used by the sample,

V_B = millilitres of silver nitrate solution used by the blank,

N = normality of the silver nitrate solution, and

W = grams of sample used.

E-3.6.8 *Precision and Accuracy*

The following criteria should be used for judging the acceptability of results:

a) *Repeatability* — Results by the same analyst should not be considered doubtful unless they differ by more than 0.006 percent or 10.5 percent of the value determined, whichever is higher.

b) *Reproducibility* — Results by different laboratories should not be considered doubtful unless they differ by more than 0.013 percent or 21.3 percent of the value detected, whichever is higher.

c) *Accuracy* — The average recovery of the method is 86 percent to 89 percent of the actual amount present.

E-4 DETERMINATION OF ANIONS BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENT (ALTERNATE METHOD)

E-4.1 Scope and Application

E-4.1.1 This method is optimized for the analysis of detrimental substances in organic based materials. It provides a single instrumental technique for rapid, sequential measurement of common anions such as bromide, chloride, fluoride, nitrate, nitrite, phosphate, and sulphate.

E-4.2 Summary of Method

E-4.2.1 The material must be put in the form of an aqueous solution before analysis can be attempted. The sample is oxidized by combustion in a bomb containing oxygen under pressure. The products liberated are absorbed in the eluent present in the bomb at the time of ignition. This solution is washed from the bomb, filtered, and diluted to a known volume.

E-4.2.1.1 A filtered aliquot of sample is injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator column). The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to weakly conductive carbonic acid. The separated anions in their acid form are measured by conductivity. They are indentified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height. Blanks are prepared and analyzed in a similar fashion.

E-4.2.2 *Interferences*

Any substance that has a retention time coinciding with that of any anion to be determined will interfere. For example, relatively high concentrations of low-molecular-weight organic acids interfere with the determination of chloride and fluoride. A high concentration of any one ion also interferes with the resolution of others. Sample dilution overcomes many interferences. To resolve uncertainties of identification or quantitation use the method of known additions. Spurious peaks may result from contaminants in reagent water, glassware, or sample processing apparatus. Because small sample volumes are used, scrupulously avoid contamination.

E-4.2.3 *Minimum Detectable Concentration*

The minimum detectable concentration of an anion is a function of sample size and conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05 mg/l for $F^-$and 0.1 mg/l for Br^-, Cl^-, NO_3^- NO_2^-,PO_4^{3-}, and SO_4^{2-} with a 100-µl sample loop and a 10-µmho full-scale setting on the conductivity detector. Similar values may be achieved by using a higher scale setting and a electronic integrator.

E-4.3 Apparatus

E-4.3.1 *Bomb*

Bomb having a capacity of not less than 300 ml, so constructed that it will not leak during the test and that quantitative recovery of the liquids from the bomb may be achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Material used in the bomb assembly, such as the head gasket and lead wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the chlorine content of the liquid in the bomb.

E-4.3.2 *Sample Cup*

Platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g; opaque fused silica, wide-form with an outside diameter of 29 mm at the top, a height of 19 mm, and a 5-ml capacity, or nickel (Kawin capsule form), top diameter of 28 mm, 15 mm in height, and 5-ml capacity.

NOTE — Fused silica crucibles are much more economical and longer lasting than platinum. After each use, they should be scrubbed out with fine, wet emery cloth, heated to dull red heat over a burner, soaked in hot water for 1 h then dried and stored in a desiccators before reuse.

E-4.3.3 *Firing Wire*

Platinum, approximately No. 26 B and S gage.

E-4.3.4 *Ignition Circuit*

This circuit shall be capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

CAUTION — The switch in the ignition circuit shall be of a type that remains open, except when held in closed position by the operator.

E-4.3.5 *Nylon Sewing Thread, or Cotton Wicking*, white.

E-4.3.6 Ion Chromatograph, including an injection valve, a sample loop, guard, separator, and suppressor columns, a temperature-compensated small-volume conductivity cell (6 µl or less), and a strip chart recorder capable of full-scale response of 2 s or less. An electronic peak integrator is optional. The ion chromatograph shall be capable of delivering 2 to 5 ml eluant/min at a pressure of 1 400 to 6 900 KPa.

E-4.3.7 *Anion Separator Column*

Anion separator column, with styrene divinyl-benzene-based low-capacity pellicular anion-exchange resin capable or resolving bromine ion, chlorine ion, fluorine ion, nitrate ion, nitrite ion, phosphate ion, and sulphate ion; 4 mm × 250 mm.

E-4.3.8 *Guard Column*

Guard column, identical to separator column except 4 mm x 50 mm, to protect separator column from fouling by particulates or organics.

E-4.3.9 *Suppressor Column*

Suppressor column, high-capacity cation-exchange resin capable of converting eluant and separated anions to their acid forms.

E-4.3.10 *Syringe*

Syringe of minimum capacity or 2 ml and equipped with a male pressure fitting.

E-4.4 Reagents

E-4.4.1 *Purity of Reagents* — Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent has sufficiently high purity to permit its use without lessening the accuracy of the determination.

E-4.4.2 *Deionized or Distilled Water*, free from interferences at the minimum detection limit of each constituent and filtered through a 0.2 µm membrane filter to avoid plugging columns.

E-4.4.3 *Eluant Solution, Sodium Bicarbonate — Sodium Carbonate* (0.003M $NaHCO_3$ — 0.0024 M Na_2CO_3)

Dissolve 1.008 g sodium bicarbonate and 1.017 6 g sodium carbonate in water and dilute to 4 litre.

E-4.4.4 *Regenerant Solution 1*, *Sulphuric Acid*, *1 N* — Use this regenerant when suppressor is not a continuously regenerated one.

E-4.4.5 *Regenerant Solution 2*, *Sulphuric Acid*, 0.025 N — Dilute 2.8 ml conc sulphuric acid (H_2SO_4) to 4 litre or 100 ml regenerant solution 1 to 4 litre. Use this regenerant with continuous regeneration fiber suppressor system.

E-4.4.6 *Standard Anion Solutions, 100 mg/ml* — Prepare a series of standard anion solutions by weighing the indicated amount of salt, dried to a constant weight at 105°C to 1 000 ml. Store in plastic bottles in a refrigerator; these solutions are stable for at least one month as indicated in Table 3.

Table 3 Standard Anion Solutions
(*Clause* E-4.4.6)

Anion	Salt	Amount g/l
CI-	NaCI	1.648 5
F-	NaF	2.210 0
Br-	NaBr	1.287 6
NO_{3-}	$NaNO_3$	1.370 7
NO_{2-}	$NaNO_2$	1.499 8
$PO4^{3-}$	KH_2PO_4	1.433 0
$SO4^{2-}$	K_2SO_4	1.814 1

E-4.4.7 *Combined Working Standard Solution, High Range* — Combine 10 ml of the Cl^-, F^-, NO_3^-, NO_2^- and PO_4^{3-} standard anion solutions. 1 ml of the Br^-, and 100 ml of the SO_4^{2-} standard solutions, dilute to 1000 mL, and store in a plastic bottle protected from light; contains 10 mg/l each Cl^-, F^-, NO_3^-, NO_2^- and PO_4^{3-}, 1 mg Br^-/l, and 100 mg SO_4^{2-}/l. Prepare fresh daily.

E-4.4.8 *Combined Working Standard Solution, Low Range* — Dilute 100 ml combined working standard solution, high range, to 1000 ml and store in a plastic bottle protected from light; contains 1.0 mg/l each Cl^-, F^-, NO_3^-, NO_2^- and PO_4^{3-}, 0.1 mg Br^-/l, and 10 mg SO_4^{2-}/l. Prepare fresh daily.

E-4.4.9 *Alternative Combined Working Standard Solutions* — Prepare appropriate combinations according to anion concentration to be determined. If NO_2^- and PO_4^{3-} and not included, the combined working standard is stable for one month.

E-4.5 Decomposition Procedure

E-4.5.1 *Preparation of Bomb and Sample*

Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Place 5 ml of sodium carbonate/sodium bicarbonate solution in the bomb, place the cover on the bomb, and vigorously shake for 15 s to distribute the solution over the inside of the bomb. Open the bomb, place the sample-filled sample cup in the terminal holder, and insert a short length of thread between the firing wire and the sample. The sample weight used should not exceed 1 g. If the sample is a solid, add a few drops of white oil at this time to ensure ignition of the sample.

E-4.5.1.1 Use of sample weights containing over 20 mg of chlorine may cause corrosion of the bomb. To avoid this it is recommended that the samples containing over 2 percent chlorine, the sample weight be based on as indicated in Table 4.

Table 4 Sample Weight with Respect to the Chlorine Content in the Sample

(*Clause* E-4.5.1.1)

Chlorine Content, percent	Sample Wight, g	White Oil Weight, g
2 to 5	0.4	0.4
5 to 10	0.2	0.6
10 to 20	0.1	0.7
20 to 50	0.05	0.7

CAUTION — Do not use more than 1 g total of sample and white oil or other fluorine-free combustible material.

E-4.5.2 *Addition of Oxygen*

Place the sample cup in position and arrange the nylon thread, or wisp of cotton so that the end dips into the sample. Assemble oxygen slowly (to avoid blowing the sample from the cup) until a pressure is reached as indicated in Table 5.

CAUTION — Do not add oxygen or ignite the sample if he bomb has been jarred, dropped, or tilted.

Table 5 Gauge Pressures

(*Clause* E-4.5.2)

Capacity of Bomb, ml	Guage Pressure, atm	
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

1) The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures present a safety requirement.

E-4.5.3 *Combustion*

Immerse the bomb in a cold-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bathe after immersion for at least 10 min. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before again putting it in use.

E-4.5.4 *Collection of Solution*

Remove the sample cup with clean forceps and rinse with deionized water and filter the washings into a 100-ml volumetric flask. Rinse the walls of the bomb shell with a fine stream of deionized water from a wash bottle, and add the washings through the filter paper to the flask. Next, rinse the bomb cover and terminals and add the washings through the filter into the volumetric flask. Finally, add deionized water to bring the contents of the flask to the line. Use aliquots of this solution for the ion chromatography (IC) analysis.

E-4.6 Procedure

E-4.6.1 *System Equilibration*

Turn on ion chromatograph and adjust eluant flow rate to approximate the separation achieved in Fig.1 (2 to 3 ml/min). Adjust detector to desired setting (usually 10 µmho) and let system come to equilibrium (15 to 20 min). A stable base line indicates equilibrium conditions. Adjust detector off-set to zero-out eluant conductivity; with the fiber suppressor adjust the regeneration flow rate to maintain stability, usually 2.5 to 3 ml/min.

E-4.6.1.1 Set up the ion chromatograph in accordance with the manufacturer's instructions.

E-4.6.2 *Calibration*

Inject standards containing a single anion or a mixture and determine approximate retention times. Observed times vary with conditions but if standard eluant and anion separator column are used, retention always in the order Fluorine ion, Chlorine ion, nitrite ion,

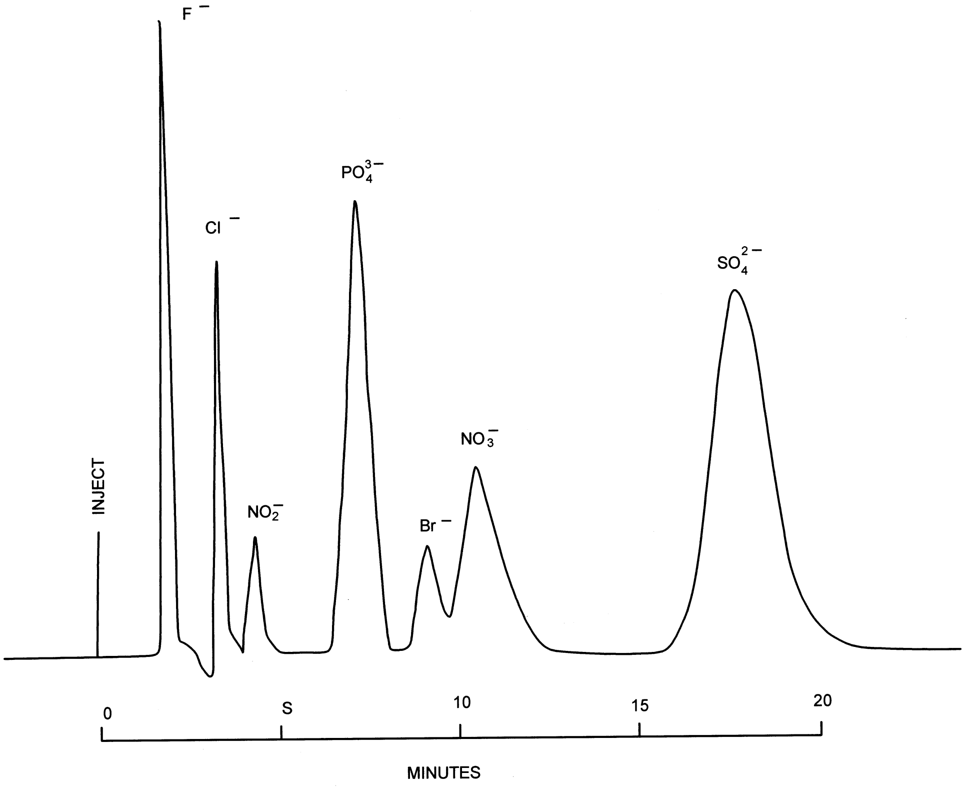

FIG. 1 TYPICAL ANION PROFILE

phosphate ion, Bromide ion, nitrate ion, and sulphate ion. Inject at least three different concentrations for each anion to be measured and construct a calibration curve by plotting peak height or area against concentration on linear graph paper. Recalibrate whenever the detector setting is changed. With a system requiring suppressor regeneration, nitrite ion interaction with the suppressor may lead to erroneous nitrite ion results; make this determination only when the suppressor is at the same stage of exhaustion as during standardization or recalibrate frequently. In this type of system the water dip (*see* caution under **E-4.5.2**) may shift slightly during suppressor exhaustion and with a fast run column this may lead to slight interference for fluorine ion or chlorine ion. To eliminate this interference, analyze standards that bracket the expected result or eliminate the water dip by diluting the sample with eluant of by adding concentrated eluant to the sample to give the same bicarbonate ion/carbonate ion concentration as in the eluant. If sample adjustments are made, adjust standards and blanks identically.

NOTE — Water dip occurs because water conductivity in sample is less than eluant conductivity (eluant is diluted by water).

E-4.6.2.1 If linearity is established for a given detector setting, it is acceptable to calibrate with a single standard. Record the peak height or area and retention time to permit calculation of the calibration factor, *F*.

E-4.6.3 *Sample Analysis*

Remove sample particulates, if necessary, by filtering through a pre-washed 0.2-µm-porediam membrane filter. Using a pre-washed syringe of 1 to 10 ml capacity equipped with a male luer fitting inject sample or standard. Inject enough sample to flush sample loop several times: for 0.1 ml sample loop inject at least 1 ml. Switch ion chromatograph from load to inject mode and record peak heights and retention.

Times on strip chart recorder. After the last peak (SO_4^{2-}) has appeared and the conductivity signal has returned to base line, another sample can be rejected.

E-4.6.4 *Regeneration*

For systems without fiber suppressor regenerate with 1 N sulphuric acid in accordance with the manufacturer's instructions when the conductivity base line exceeds 300 µmho when the suppressor column is on line.

E-4.7 Calculation

E-4.7.1 Calculate concentration of each anion, in mg/l, by referring to the appropriate calibration curve. Alternatively, when the response is shown to be linear, use the following equation:

$$C = H \times F \times D$$

where

C = mg anion/l,

H = peak height or area,

F = response factor – concentration of standard/ height (or area) of standard, and

D = dilution factor for those samples requiring dilution.

E-4.8 Precision and Bias

E-4.8.1 Samples or reagent water to which were added the common anions were analyzed in 15 laboratories with the results shown in Table 6.

Table 6 Precision and Accuracy Observed for Anions at Various Concentration Levels in Reagent Water

(*Clause* E-4.8.1)

Anion	Amount Added	Amount Found	Overall Precision	Single operator Precision	Significant Bias 95 percent
	mg/l	mg/l	mg/l	mg/l	Level
F-	0.48	0.49	0.05	0.03	No
F-	4.84	4.64	0.52	0.46	No
Cl	0.76	0.86	0.38	0.11	No
Cl-	17	17.2	0.82	0.43	No
Cl	455	471	46	13	No
NO_2	0.45	0.09	0.09	0.04	Yes, neg
NO_2	21.8	19.4	1.9	1.3	Yes, neg
Br-^{2}	0.25	0.25	0.04	0.02	No
Br-	13.7	12.9	1.0	0.6	No
PO_4^3-	0.18	0.10	0.06	0.03	Yes, neg
PO_4^3-	0.49	0.34	0.15	0.17	Yeas, neg
NO_3-	0.50	0.33	0.16	0.03	No
NO_3-	15.1	14.8	1.15	0.9	No
SO_4^2-	0.51	0.52	0.07	0.03	No
SO_4^2-	43.7	43.5	2.5	2.2	No

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Headquarters:

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Eastern : 1/14 C.I.T. Scheme VII M, V. I. P. Road, Kankurgachi
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